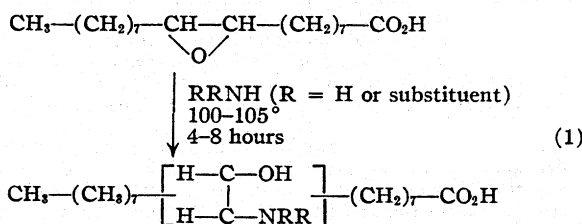


# Chemistry of Epoxy Compounds. XIV.<sup>1</sup> Reaction of *cis*-9,10-Epoxyoctadecaric Acid with Ammonia and Amines<sup>2</sup>

By DANIEL SWERN AND THOMAS W. FINDLEY

This note reports the opening of the oxirane ring of *cis*-9,10-epoxyoctadecaric acid with ammonia and amines (equation 1), the isolation of pure 9,10(10,9)-aminohydroxyoctadecaric acid and moderately pure *N*-substituted aminohydroxyoctadecaric acids, and potentiometric titration curves for several of these amino acids in the presence and absence of formaldehyde.



## Experimental

**Materials Used.**—*cis*-9,10-Epoxyoctadecaric acid, m.p. 59.5°, was prepared from oleic acid by epoxidation with perbenzoic acid.<sup>3</sup> A.C.S. reagent grade concentrated aqueous ammonia was used. The Eastman Kodak Co. White Label Grades of 25% aqueous methylamine, 33% aqueous ethylamine, 33% aqueous dimethylamine and diethylamine were used without further purification. Diethylamine was diluted with approximately two parts of water to yield a 33% solution. Aniline was freshly distilled before use.

**Preparation of 9,10(10,9)-Aminohydroxyoctadecaric Acid.**—A typical experiment is described. Six grams (0.02 mole) of 9,10-epoxyoctadecaric acid and 14 ml. of 14.5 *N* aqueous ammonia (0.20 mole) were placed in a Pyrex glass combustion tube sealed at one end and partially constricted at the other. The tube was immersed in Dry Ice-acetone for several minutes and the constricted end of the tube was sealed off. The tube was then placed within a steel pipe which was closed with threaded caps at each end, and the whole assembly was heated and rotated in an oil-bath at 100–105° for four hours. The steel pipe was removed from the bath and allowed to cool to room temperature. The glass tube was again immersed in Dry Ice for several minutes and the tube was opened. The contents were transferred quantitatively to an evaporating dish and 205 ml. of 0.1 *N* aqueous sodium hydroxide was added. The solution was boiled until the odor of ammonia could not be detected and the vapors gave no test for alkalinity with test paper (about one to two hours were required). Sufficient (approximately 205 ml.) 0.1 *N* hydrochloric acid was then added to neutralize the sodium hydroxide and yield a mixture whose pH was about 6. A viscous oil precipitated which solidified on standing overnight; weight 6.1 g. The crude 9,10(10,9)-aminohydroxyoctadecaric acid was crystallized twice from 95% ethanol (8 ml./g.) at 0°, yielding 3.5 g. (55%) of pure material, m.p. 153–155°. In duplicate experiments, yields ranging from 30–62% were obtained. *Anal.* Calcd. for  $\text{C}_{18}\text{H}_{37}\text{O}_4\text{N}$ : C, 68.6; H, 11.8; N, 4.44; neut. equiv., 315.5. Found: C, 68.9; H, 11.7; N, 4.51; neut. equiv. (formaldehyde present), 316.

**Preparation of *N*-Substituted 9,10(10,9)-Aminohydroxyoctadecaric Acids.**—The reaction of aqueous methylamine (12.4 g.) with *cis*-9,10-epoxyoctadecaric acid (6.0 g.) for eight hours at 100–105° yielded a viscous oil which did not solidify after removal of excess methylamine and acidification, as described in the preceding section under 9,10(10,9)-aminohydroxyoctadecaric acid. The reaction product was evaporated to dryness and separated from sodium chloride by solution in 40 ml. of boiling absolute ethanol. The ethanol solution was cooled to –50° for one week, yielding 1 g. of 9(10)-*N*-

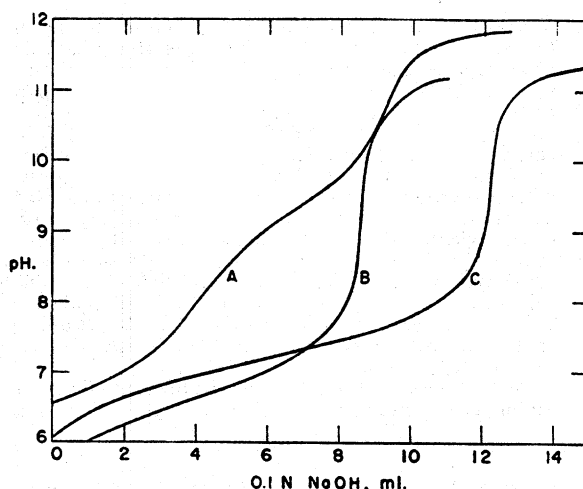


Fig. 1.—Titration curves for 9,10(10,9)-aminohydroxyoctadecaric acid: A, 0.3270 g. of pure sample, formaldehyde absent; B, 0.2720 g. of pure sample, formaldehyde present; neut. equiv., 316 (8.61 ml. of 0.1 *N* NaOH required); C, 0.4162 g. of crude reaction product, formaldehyde present; neut. equiv., 340 (12.24 ml. of 0.1 *N* NaOH required).

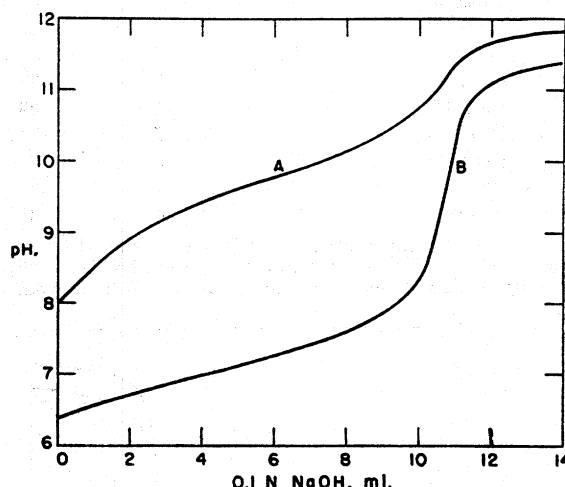


Fig. 2.—Titration curves for 9(10)-*N*-methylamino-10(9)-hydroxyoctadecaric acid: A, 0.3722 g. of sample, formaldehyde absent; B, 0.3563 g. of sample, formaldehyde present; neut. equiv., 330 (10.80 ml. of 0.1 *N* NaOH required).

methylamino-10(9)-hydroxyoctadecaric acid, m.p. 100–103°. *Anal.* Calcd. for  $\text{C}_{19}\text{H}_{39}\text{O}_4\text{N}$ : N, 4.25; neut. equiv., 329.5. Found: N, 4.59; neut. equiv. (formaldehyde present), 331.5. The filtrate was evaporated to dryness yielding 5 g. of viscous oil; N, 4.19; neut. equiv., 348. It was evident, therefore, that the reaction yielded mainly 9(10)-*N*-methylamino-10(9)-hydroxyoctadecaric acid.

Aqueous ethylamine (13.7 g.) and *cis*-9,10-epoxyoctadecaric acid (6.0 g.) yielded 7.3 g. of a viscous oil after separation of the sodium chloride as described above. *Anal.* Calcd. for 9(10)-*N*-ethylamino-10(9)-hydroxyoctadecaric acid,  $\text{C}_{20}\text{H}_{41}\text{O}_4\text{N}$ : N, 4.08. Found: N, 4.36. No precipitate was obtained when a solution of this product in absolute ethanol was cooled to –50°.

Aqueous dimethylamine (13.7 g.) and *cis*-9,10-epoxyoctadecaric acid (6.0 g.) yielded 7.7 g. of yellow viscous oil from the alcohol solution. *Anal.* Calcd. for 9(10)-*N,N*-dimethylamino-10(9)-hydroxyoctadecaric acid,  $\text{C}_{20}\text{H}_{41}\text{O}_4\text{N}$ : N, 4.08. Found: N, 3.67. This product showed appreciable water solubility; a 5% solution was only slightly turbid.

Aqueous diethylamine (21 g.) and *cis*-9,10-epoxyoctadecaric acid (6.0 g.) yielded 7.1 g. of a semi-solid. *Anal.* Calcd. for 9(10)-*N,N*-diethylamino-10(9)-hydroxyoctadecaric acid,  $\text{C}_{22}\text{H}_{45}\text{O}_4\text{N}$ : N, 3.77. Found: N, 2.64.

(1) For paper XIII, see *THIS JOURNAL*, **74**, 1655 (1952).

(2) Article not copyrighted.

(3) D. Swern, T. W. Findley and J. T. Scanlan, *THIS JOURNAL*, **66**, 1925 (1944).

*cis*-9,10-Epoxyoctadecanoic acid (24 g., 0.08 mole) and aniline (72 g., 0.8 mole) were heated on the steam-bath for six hours in a nitrogen atmosphere. The reaction mixture was poured into 1 liter of 1.5 *N* hydrochloric acid in a separatory funnel and the aqueous layer was discarded. The upper oil layer was washed with four 500-ml. portions of 1.5 *N* hydrochloric acid, then with 5% sodium chloride until the wash was neutral, and twice with distilled water. The upper layer was dissolved in ethyl acetate and the solution was dried over anhydrous calcium sulfate. Filtration and evaporation of solvent yielded 16–25 g. of reddish-brown oil. Analysis indicated that it contained about 80% 9(10)-*N*-phenylamino-10(9)-hydroxyoctadecanoic acid and about 20% of the anilide of this substance. *Anal.* Calcd. for 9(10)-*N*-phenylamino-10(9)-hydroxyoctadecanoic acid,  $C_{24}H_{41}O_3N$ : N, 3.57; neut. equiv., 391.5; calcd. for the anilide,  $C_{30}H_{46}O_2N_2$ : N, 6.0. Found: N, 4.05; neut. equiv., 475–481.

**Surface Active Properties of *N*-Substituted 9(10),10(9)-Aminohydroxyoctadecanoic Acids.**—Although 9(10)-*N*,*N*-di-

methylamino-10(9)-hydroxyoctadecanoic acid was the only compound studied which showed appreciable water solubility, 9(10)-*N*-methylamino- and 9(10)-*N*-ethylamino-10(9)-hydroxyoctadecanoic acids showed slight solubility. Surface tensions of 0.2% solutions of these compounds under neutral, acidic and alkaline conditions are shown in Table I. Measurements were made with the Du Nouy Interfacial Tensiometer.

**Potentiometric Titrations.**—Approximately 0.3–0.6 g. of *N*-substituted or unsubstituted aminohydroxyoctadecanoic acids were dissolved in 100 ml. of 70% aqueous ethanol and the titration curves were determined using a pH meter with external electrodes. With the exception of the titration of 9(10)-*N*-phenylamino-10(9)-hydroxyoctadecanoic acid, the compounds studied showed no sharp inflection in the titration curves if formaldehyde was absent from the titration mixture. To obtain satisfactory titration curves, it was necessary to employ formaldehyde. Approximately 10 ml. of 35% aqueous formaldehyde, neutralized with dilute aqueous alkali to phenol red, was used in the solvent system. Figure 1 shows the titration curves for pure 9(10),10(9)-aminohydroxyoctadecanoic acid in the absence (A) and presence (B) of formaldehyde, and the crude reaction product of *cis*-9,10-epoxyoctadecanoic acid with aqueous ammonia prior to recrystallization (C, formaldehyde present). Figure 2 shows the titration curves for 9(10)-*N*-methylamino-10(9)-hydroxyoctadecanoic acid in the absence (A) and presence (B) of formaldehyde and Fig. 3, curves A and B, show similar data for 9(10)-*N*-phenylamino-10(9)-hydroxyoctadecanoic acid.

### Discussion

With the exception of 9(10)-*N*-phenylamino-10(9)-hydroxyoctadecanoic acid, the titration curves in the absence of formaldehyde show that substituted and unsubstituted aminohydroxyoctadecanoic acids behave as typical amino acids, namely, they exist in solution as salts even in 70% ethanol. Formaldehyde, since it suppresses the basic properties of the nitrogen, permits a typical titration curve to be obtained. The failure of 9(10)-*N*-phenylamino-10(9)-hydroxyoctadecanoic acid to show any difference in behavior in the absence or presence of formaldehyde is attributed to the lower basic strength of nitrogen containing a phenyl substituent, thereby preventing salt formation from occurring.

The relatively high water-solubility of 9(10)-*N*,*N*-dimethylamino-10(9)-hydroxyoctadecanoic acid is attributed to the higher basic strength of the dimethylamino moiety, which would enhance salt formation and, consequently, solubility in water. The surface-active properties of the compounds are to be expected in view of their salt formation and structural relationship to amine salts of long-chain fatty acids in which properly balanced hydrophilic and hydrophobic groups are present. Sinking time measurements on canvas disks immersed in aqueous solutions of these substances show that the canvas is penetrated rapidly but not nearly so rapidly as in aqueous solutions of the sodium salt of dioctyl sulfosuccinate of the same concentration.

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TABLE I

SURFACE TENSION OF 0.2% SOLUTIONS OF *N*-SUBSTITUTED 9,10(9,9)-AMINOHYDROXYOCTADECANOIC ACIDS

Aminohydroxyoctadecanoic acid	<i>t</i> , °C.	pH <sup>a</sup>	Surface tension, dynes/cm.
Dimethyl-	19	4	36
Dimethyl-	19	7	33
Dimethyl-	19	9	38
Dimethyl-	19	11	37
Methyl-	24	4	36
Methyl-	24	7	33
Methyl-	24	9	38
Methyl-	24	11	39
Methyl- <sup>b</sup>	24	7	34
Ethyl-	24	5	37
Ethyl-	24	7	33
Ethyl-	24	10	36

<sup>a</sup> The pH values other than 7 were obtained by the addition of a sufficient quantity of aqueous sodium hydroxide or hydrochloric acid. <sup>b</sup> Half-saturated with sodium chloride.

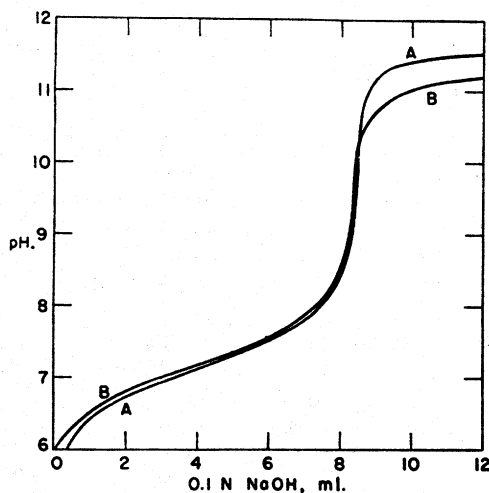


Fig. 3.—Titration curves for 9(10)-*N*-phenylamino-10(9)-hydroxyoctadecanoic acid: A, 0.4014 g. of sample, formaldehyde absent; neut. equiv., 475 (8.45 ml. of 0.1 *N* NaOH required); B, 0.4024 g. of sample, formaldehyde present; neut. equiv., 481 (8.37 ml. of 0.1 *N* NaOH required).